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Effect of Vanadium Substitution on Structure of $\text{Li}_2\text{FeSiO}_4/\text{C}$ Composites

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Abstract: The carbon coated lithium iron silicate ($\text{Li}_2\text{FeSiO}_4/\text{C}$) composites were prepared using less expansive iron starting material of soluble ferric nitrate through sol-gel process and solid state reaction. The theoretically calculated amounts of 5%, 10%, 15%, 20%, 25%, 30%, and 50% of vanadium (V) were introduced using NH_4VO_3 to obtain V-substituted $\text{Li}_2\text{FeSiO}_4/\text{C}$ composites. It was found that the pure $\text{Li}_2\text{FeSiO}_4/\text{C}$ composite exhibited a good crystallinity with $P2_1/n$ and nearly no impurities being detected, while the V-substituted $\text{Li}_2\text{FeSiO}_4/\text{C}$ composites showed major impurities of Li_2SiO_3 and $\text{V}_3\text{O}_4/\text{Fe}_3\text{O}_4$. The discharge capacities of $160.9 \text{ mAh} \cdot \text{g}^{-1}$ and $130.8 \text{ mAh} \cdot \text{g}^{-1}$ at C/16 were obtained for the pure and 5% V-substituted $\text{Li}_2\text{FeSiO}_4/\text{C}$ composites, respectively. The degree of graphitization in amorphous carbon was enhanced and the quantities of carbon coated were lowered with the increase of V-substituted amounts. The electrochemical performance of 5% V-substituted $\text{Li}_2\text{FeSiO}_4/\text{C}$ composite was not improved due to the presences of impurities which were directly linked to the amounts of V substitution.

Key words: lithium iron silicates; vanadium substitution; cathode materials; lithium ion battery

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The polyanion-type cathode material of $\text{Li}_2\text{FeSiO}_4$ is considered as one of the most promising cathode materials for lithium ion batteries because of its excellent structural stability, good reliability and high performance with a nominal capacity of $330 \text{ mAh} \cdot \text{g}^{-1}$ upon two lithium ions being extracted. However, low intrinsic electrical conductivity and poor discharge capability at large current^[1] have limited its practical applications. It has been reported that carbon coating^[2], doping or substitution by metal cations^[3] and control of surface morphologies^[4] could effectively enhance the electrochemical performances of $\text{Li}_2\text{FeSiO}_4$. The electrical conductivities of $\text{Li}_2\text{FeSiO}_4$ were increased either directly by changing electric structures through metal doping/substitution or indirectly by lowering contact resistances of active particle surfaces through carbon coating^[5].

Doping or substitution with some transition met-

al cations including Mg^{2+} ^[5], Cu^{2+} and Zn^{2+} ^[6], Mn^{2+} ^[7-8], Ni^{2+} ^[9], or Cr^{2+} ^[10] in $\text{Li}_2\text{FeSiO}_4$ has been extensively investigated. However, vanadium(V) modifications are less studied. Diversified valence states of V and difficulties in identifications of V presented after doping/substitution lead to complexities and varieties of V existing forms. Compared with metal doping which is usually introduced $\leq 5\%$ into cathode materials, metal substitutions ($>5\%$) are considered to be a more efficient way to control structure and property of materials. Recently, it has been demonstrated through the first-principles calculation by GGA+U, the specific energy density of $978 \text{ Wh} \cdot \text{kg}^{-1}$ could be achieved by substituting 50% V^{2+} for the same amount of Fe^{2+} to form $\text{Li}_2\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4$ which facilitates the extraction of second lithium ions^[11]. An experimental effort was also made to prepare 10% V-substituted $\text{Li}_2\text{FeSiO}_4$ ^[12]. Based on the rough analy-

ses of XRD and XPS data, it was found that the electrochemical performance of 10% V-substituted $\text{Li}_2\text{FeSiO}_4$ got even worse due possibly to the lithium deficient formed by substitutions of V^{3+} for Fe^{2+} [12]. It is, therefore, necessary to clarify possible forms/states of V introduced into $\text{Li}_2\text{FeSiO}_4$ materials through V substitution in order to achieve high capacity by effectively removing two lithium ions.

In this work, a series of V-substituted $\text{Li}_2\text{FeSiO}_4/\text{C}$ composites were prepared through sol-gel process and solid state reaction to systematically study the effect of the amounts of V-substitutions on the structure of $\text{Li}_2\text{FeSiO}_4/\text{C}$ composites. The crystal structure, carbon phase and carbon coated amount of V-substituted materials were characterized by XRD, FT-IR, Raman spectroscopy and elemental analyzer. The main objective of this work was intended to provide fundamental understanding in structural change of cathode materials by V substitutions.

1 Experimental

1.1 Preparation of $\text{Li}_2\text{FeSiO}_4/\text{C}$ Composites

Stoichiometric amounts of analytical grade $\text{CH}_3\text{COOLi} \cdot 2\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were mixed thoroughly in ethanol at 50 °C for 2 h. The tetraethylorthosilicate (TEOS, AR) and acetic acid (as a catalyst, AR) were added into the as-prepared solution under magnetic stirring. The mixtures were then refluxed at 80 °C until the ethanol was evaporated. The resulting precursors were mixed with sucrose (AR) and acetone (AR), and then ground for 12 h by ball milling with a rotation speed of 400 $\text{r} \cdot \text{min}^{-1}$. After the evaporation of acetone, thorough grinding the xerogel with the mortar and pestle, the obtained powders were pressed into pellets and then transferred into the oven. The pellets were calcined at 650 °C for 10 h under the fixed flowing of N_2 ($\geq 99.999\%$) to yield the final products of $\text{Li}_2\text{FeSiO}_4/\text{C}$ composites. Different amounts of V-substituted $\text{Li}_2\text{FeSiO}_4/\text{C}$ composites were prepared by introducing 5%, 10%, 15%, 20%, 25%, 30% and 50% of NH_4VO_3 (AR), respectively.

1.2 Characterizations of $\text{Li}_2\text{FeSiO}_4/\text{C}$ Composites

The crystal structures were determined by X-ray diffraction (XRD, Panalytical X'pert PRO) with a $\text{Cu-K}\alpha$ radiation source operated at 40 kV and 30 mA. The data were recorded in the 2θ range of $10^\circ \sim 80^\circ$ with a step size of $\sim 0.02^\circ$ and a constant counting time of 12 s per step. Raman spectra (TriVista CRS557) were collected from 240 to 1820 cm^{-1} using 325 nm ultraviolet radiation. The surface species were further identified by Fourier transformed infrared spectroscopy (FTIR, Nicolet Avatar 360). The amount of carbon presented in the V-substituted $\text{Li}_2\text{FeSiO}_4/\text{C}$ composites was determined by elemental analyzer (Vario EL III).

Electrochemical performances of pure and different vanadium substituted $\text{Li}_2\text{FeSiO}_4/\text{C}$ composites were investigated using a CR2016 coin-type cell. The geometrical area of the electrode was 2 cm^2 . To prepare the cathode, active material, super-p and PTFE 60% binder were mixed according to the ratio of 80:10:10 by weight. The cells were assembled in an argon-filled glove box with pre-prepared cathode, lithium metal as the anode and Celgard 2400 as the separator. The electrolytes were 1 $\text{mol} \cdot \text{L}^{-1}$ LiPF_6/EC and DEC(1:1, by volume). The loading densities of the electrodes were 5.0 $\text{mg} \cdot \text{cm}^{-2}$. The galvanostatic charge-discharge measurements were performed in a potential range of 1.5 ~ 4.8 V at room temperature by Land CT2001A battery test system (Wuhan, China). The capacity was calculated on the basis of the active material, that is, the mass of the $\text{Li}_2\text{FeSiO}_4$.

2 Results and Discussion

Typical XRD patterns of pure and 5% V-substituted $\text{Li}_2\text{FeSiO}_4/\text{C}$ composites are compared in Fig. 1. Both data showed strong backgrounds in Bragg reflection, implying the presence of amorphous carbon in the composites. Based on three crystal structures of $\text{Li}_2\text{FeSiO}_4$, namely, $Pmnb$ [13], $Pmn2_1$ [14] and $P2_1/n$ [15], reported according to theoretical calculations, the main crystalline phases for both pure and 5% V-substituted $\text{Li}_2\text{FeSiO}_4/\text{C}$ composites were determined to be $P2_1/n$ as evident by a strong peak at $2\theta \approx 24.3^\circ$ along with the three consecutive minor peaks in the range of $20^\circ \sim 25^\circ$. No apparent impurities were observed

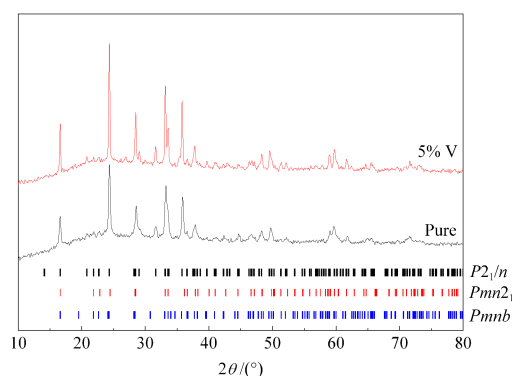


Fig. 1 Typical XRD patterns of pure and 5% V-substituted $\text{Li}_2\text{FeSiO}_4/\text{C}$ composites

from the $\text{Li}_2\text{FeSiO}_4/\text{C}$ composite obtained without V substitution, while the main impurities of Li_2SiO_3 (JCPDS 29-0829) and V_3O_4 (JCPDS 34-0615) or Fe_3O_4 (JCPDS-65-3107) were also found for the 5% V-substituted $\text{Li}_2\text{FeSiO}_4/\text{C}$ composite.

The initial charge-discharge curves of pure and 5% V-substituted $\text{Li}_2\text{FeSiO}_4/\text{C}$ cathode materials at ambient temperature and C/16 are given in Fig. 2A. The first discharge capacity of the pure $\text{Li}_2\text{FeSiO}_4/\text{C}$ reached $148.6 \text{ mAh} \cdot \text{g}^{-1}$ with two charge-discharge platforms of 3.2 V and 2.5 V, while that of the 5% V-substituted $\text{Li}_2\text{FeSiO}_4/\text{C}$ reached $122.9 \text{ mAh} \cdot \text{g}^{-1}$ with the charge-discharge platforms of 3.6 V and 2.2 V. The cycling performance and Coulombic efficiency shown in Fig. 2B revealed that the maximum discharge capacities of 160.9 at 27 cycles and $130.8 \text{ mAh} \cdot \text{g}^{-1}$ at 24 cycles were obtained, while $147.4 \text{ mAh} \cdot \text{g}^{-1}$ (91.6% remained) and $126.3 \text{ mAh} \cdot \text{g}^{-1}$ (96.6%

remained) could be maintained upon 41 cycles for both pure and 5% V-substituted $\text{Li}_2\text{FeSiO}_4/\text{C}$ cathode materials, respectively. Almost 100% Coulombic efficiencies were achieved for both pure and 5% V-substituted $\text{Li}_2\text{FeSiO}_4/\text{C}$ cathode materials. The substitution of 5% V into $\text{Li}_2\text{FeSiO}_4/\text{C}$ seemed not to increase the discharge capacity, but slightly improve the cycling performance.

To more systematically examine the effect of V substitution on the structure of $\text{Li}_2\text{FeSiO}_4/\text{C}$ composites, a series of different amounts of V-substituted (up to 50%) $\text{Li}_2\text{FeSiO}_4/\text{C}$ composites were prepared. The obtained XRD data are given in Fig. 3A. Compared with the pure $\text{Li}_2\text{FeSiO}_4/\text{C}$ composite, the V substitutions resulted in the apparent intensity weakness of characteristic peaks associated with the $P2_1/n$ $\text{Li}_2\text{FeSiO}_4$ and presences of such impurities as Li_2SiO_3 and $\text{V}_3\text{O}_4/\text{Fe}_3\text{O}_4$. A closer examination in the XRD data ranging from $34^\circ \sim 37^\circ$, as seen in Fig. 3B, revealed that common impurities such as Fe_3O_4 might also be simultaneously presented since the characteristic peaks of V oxides and Fe oxides can not be readily differentiated from each other based on the XRD data. Therefore, M_xO_y ($\text{M}=\text{Fe}, \text{V}$) is used to represent metal oxides in the following quantitative analysis.

As illustrated in Fig. 3B, the Bragg reflection peak associated with M_xO_y ($\sim 35.2^\circ$) gradually developed with the increase in the amounts of V substitution, and eventually became a strong and well-defined peak, while that observed near 35.7° gradually weakened, and finally disappeared upon the substitu-

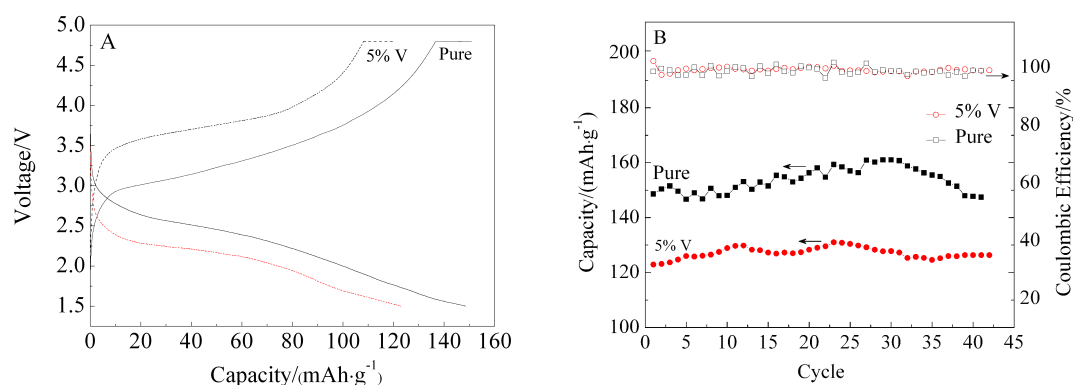


Fig. 2 Initial charge-discharge curves (A) and cycling performance as well as Coulombic efficiency (B) of pure and 5% V-substituted $\text{Li}_2\text{FeSiO}_4/\text{C}$ cathode materials at ambient temperature and C/16

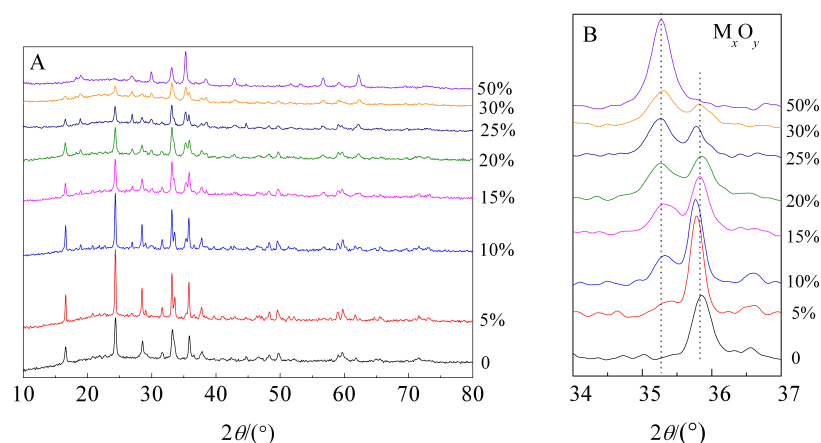


Fig. 3 XRD patterns of $\text{Li}_2\text{FeSiO}_4/\text{C}$ composites prepared without and with different amounts of V substitution (A) and an expanded view of selected XRD data in the range of $34^\circ \sim 37^\circ$ (B)

tion of 50% V. Since a linear relationship between the amount of phase and the related peak intensity/area in the same series of XRD spectra^[16], quantitative analyses were performed by carefully multi-curve fitting of the reflection peaks corresponding to M_xO_y . The relative intensities in the integrated areas of the M_xO_y peaks with the total integrated areas below the M_xO_y peaks were used to represent the amounts of M_xO_y being formed in the composites. The fitting results are provided in Fig. 4. Apparently, the formation of M_xO_y depended linearly on the amounts of V substitution, which greatly suppressed the formation of $\text{Li}_2\text{FeSiO}_4$ and introduced more impurities.

A comparison of FT-IR data obtained with different V substitutions is presented in Fig. 5. It can be

seen from $\text{Li}_2\text{FeSiO}_4/\text{C}$ that the characteristic peaks observed near 444 cm^{-1} were related to the bending vibration of O—Li—O for LiO_4 tetrahedra, while 524 and 582 cm^{-1} belonged to the bending vibration of O—Si—O , 893 and 931 cm^{-1} to the stretching vibration of Si—O for SiO_4 tetrahedra^[17]. The peaks developed around 735 and 1067 cm^{-1} corresponded to the asymmetric stretching vibration of Si—O—Si and stretching vibration of O=Si—O ^[18], respectively, from the impurities of Li_2SiO_3 by V substitutions. The appearance of IR peaks at 512 and 983 cm^{-1} might be associated with the bending vibration of V—O—V and stretching vibration of V=O ^[19], respectively, due to the formation of V_2O_5 by V substitutions larger than 25%. The FT-IR results were consistent with the XRD. However, the formation of iron oxides could

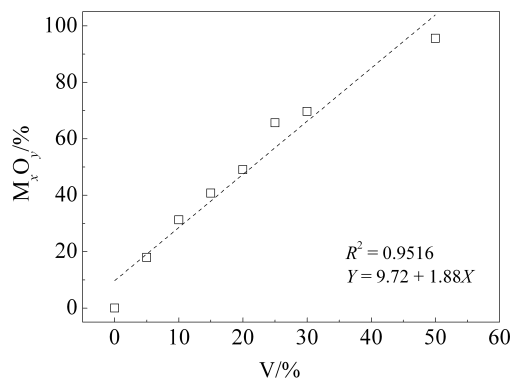


Fig. 4 A linear fit of the integrated area of the corresponding Bragg reflection for M_xO_y

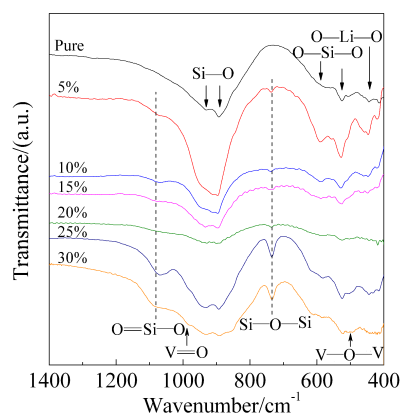


Fig. 5 FT-IR patterns of $\text{Li}_2\text{Fe}_{1-x}\text{V}_x\text{SiO}_4/\text{C}$

not be confirmed with the FT-IR spectra.

The effects of V substitutions on carbon coatings were evaluated by the degree of graphitization indicated by I_D/I_G based on Raman data and the amount of carbon (C%) obtained from elemental analyzer. The results are shown in Fig. 6. It seemed that both the I_D/I_G and C% values were noticeably affected by the V substitutions. The reduced I_D/I_G values (Fig. 6A) might be related to the improved degree of graphitization and larger particle sizes by V substitutions, while the C% values decreased first then slightly increased with increasing the amounts of V substitution, and became less influenced upon 20% or higher V substitutions. Therefore, V substitutions influenced not only the crystal structure, but also the carbon phase presented in the $\text{Li}_2\text{FeSiO}_4/\text{C}$ composites. With the increasing amounts of V substitution, more impurities including metal oxides ($\text{V}_3\text{O}_4/\text{Fe}_3\text{O}_4$) were formed and the degree of amorphous carbon became more graphitized accompanied with lower weight percentages of carbon coated.

3 Summary

The pure and a series of V-substituted $\text{Li}_2\text{FeSiO}_4/\text{C}$ composites were synthesized using sol-gel and solid state reaction methods. The XRD patterns indicated

that almost no impurities with main phase of $P2_1/n$ were observed for the pure $\text{Li}_2\text{FeSiO}_4/\text{C}$ composite, while major impurities of Li_2SiO_3 and metal oxides ($\text{V}_3\text{O}_4/\text{Fe}_3\text{O}_4$) for the V-substituted $\text{Li}_2\text{FeSiO}_4/\text{C}$ composites. As the amounts of V substitution increased, the quantities of $\text{V}_3\text{O}_4/\text{Fe}_3\text{O}_4$ formation increased linearly, the degree of graphitization in amorphous carbon was enhanced and the amount of carbon coated was reduced. The discharge capacities of $160.9 \text{ mAh} \cdot \text{g}^{-1}$ and $130.8 \text{ mAh} \cdot \text{g}^{-1}$ at C/16 were obtained for the pure and 5% V-substituted $\text{Li}_2\text{FeSiO}_4/\text{C}$ composites, respectively. The presences in a large amount of impurities with V substitutions might cause the poorer electrochemical performance of 5% V-substituted $\text{Li}_2\text{FeSiO}_4/\text{C}$ composite.

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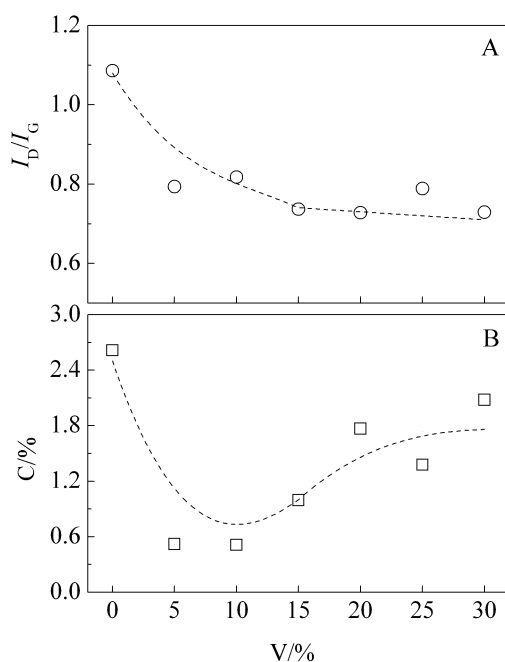


Fig. 6 I_D/I_G and C% as a function of V substitution

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钒替代对碳包覆硅酸铁锂复合材料结构的影响

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摘要: 以廉价硝酸铁为铁原料, 通过溶胶-凝胶和固相反应法制得碳包覆硅酸铁锂($\text{Li}_2\text{FeSiO}_4/\text{C}$)正极材料。以偏钒酸铵(NH_4VO_3)为钒原料, 按理论计算量 5%、10%、15%、20%、25%、30% 和 50% 制得钒替代 $\text{Li}_2\text{FeSiO}_4/\text{C}$ 复合材料($\text{Li}_2\text{Fe}_{1-x}\text{V}_x\text{SiO}_4/\text{C}$)。结果表明, $\text{Li}_2\text{FeSiO}_4/\text{C}$ (主相 $P2_1/n$) 结晶良好, 基本无杂相, 而 $\text{Li}_2\text{Fe}_{1-x}\text{V}_x\text{SiO}_4/\text{C}$ (主相 $P2_1/n$) 存在主要杂质偏硅酸锂和钒/铁氧化物。 $\text{Li}_2\text{FeSiO}_4/\text{C}$ 和 $\text{Li}_2\text{Fe}_{0.95}\text{V}_{0.05}\text{SiO}_4/\text{C}$ 电极 C/16 (室温) 的首次放电比容量分别达 $160.9 \text{ mAh} \cdot \text{g}^{-1}$ 和 $130.8 \text{ mAh} \cdot \text{g}^{-1}$ 。钒替代量增加, 无定形碳的石墨化程度增强, 碳包覆量却减少。钒替代量直接影响钒/铁氧化物的形成量, 导致 $\text{Li}_2\text{Fe}_{0.95}\text{V}_{0.05}\text{SiO}_4/\text{C}$ 电极电化学性能较差。

关键词: 硅酸铁锂; 钒取代; 正极材料; 锂离子电池